[Second Edition.]

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Butadiene from Butane.

We, I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany, do hereby declare the nature of this invention and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement :—

It has already been proposed to prepare butadiene from butane by direct thermal dehydrogenation. Only very moderate yields of butadiene are, however, obtained by this process.

We have now found that butadiene is obtained in good yields by the dehydrogenation of butane by converting the butane by heating in the presence of dehydrogenation catalysts into butylene, isolating the latter from the reaction mixture, further dehydrogenating it to butadiene and isolating the butadiene from the products of the dehydrogenation. The further treatment of the dehydrogenation product containing butylene first obtained leads to only small yields of butadiene.

The conversion of butane into butylene is preferably effected at temperatures of from 500° to 600° Centigrade while using activated aluminium oxide. Oxides of chromium, vanadium, tungsten and molybdenum are especially suitable as activating agents. It is preferable to work under such conditions that only up to about 35 *per cent.* of the butane is converted into butylene. The butylene formed is washed out from the reaction gases with solutions or suspensions of salts which absorb olefines, in particular silver, copper or mercurous nitrate solutions. The butylene, which is present in the solutions or suspensions as addition compounds, is set free by heating or evacuation. It is usually sufficiently pure for the further use. If necessary it may be purified, for example by fractional distillation. The unchanged butane is again subjected to dehydrogenation in a cycle.

The butylene obtained is then dehydrogenated to butadiene in the presence or absence of catalysts. In this case also it is preferable to convert only up to about 30 *per cent.* of the butylene into butadiene in one operation. From the resulting reaction mixture, the butadiene is washed out with solutions of salts of the heavy metals of groups 1 or 2 of the periodic system, in particular cuprous chloride solutions, which preferably contain ammonium or alkali chloride. The butadiene obtained is especially readily polymerisable and yields high quality rubber because it is free from substances preventing or hindering polymerisation.

The following Example will further illustrate how the said invention may be carried out in practice, but the invention is not restricted to this Example. The parts are by volume.

EXAMPLE.

Normal-butane is led at atmospheric pressure over a dehydrogenation catalyst heated to from 500° to 520° Centigrade and consisting of 95 *per cent.* of aluminium oxide and 5 *per cent.* of chromium oxides, at such a speed that by a single passage from 30 to 35 *per cent.* of butylene is formed. (The chromium oxides used in the catalyst may be prepared by reducing chromic acid in a current of hydrogen, or a mixture of aluminium oxide and chromium oxides may be prepared by reducing aluminium chromate in a current of hydrogen. This mixture is then admixed with further amounts of aluminium oxide). The dehydrogenation of the butane to butylene thus proceeds without appreciable formation of bye-products.

The gas mixture obtained is freed from butylene by washing with concentrated, about 50 *per cent.*, silver nitrate solution and the unchanged butane is again subjected to dehydrogenation in a cycle. By heating the silver nitrate solution, the butylene is set free. It contains butane only in traces and may usually be directly used. If desired it may be completely purified by repeated treatment with silver nitrate solution or by fractional distillation.

The butylene is then led diluted with 10 parts of carbon dioxide through a chamber filled with porcelain balls or quartz pieces at 680° Centigrade at such a speed

[*Price*

that from 25 to 30 *per cent.* of butadiene are formed by a single passage. The gases leaving the catalytic chamber are freed from butadiene by washing with an aqueous solution of cuprous chloride and ammonium chloride and returned again to the catalytic chamber. From the resulting complex compound of butadiene and cuprous chloride and ammonium chloride, the butadiene is set free and, if necessary, purified by distillation.

We are aware of specification No. 481,646 which describes and claims a process for producing butadiene comprising catalytically dehydrogenating normal butane without substantial formation of butadiene in one step, followed by catalytically dehydrogenating a portion of the butylene to butadiene in a second step, removing the butadiene so formed and recirculating the remaining hydrocarbons of four carbon atoms for further dehydrogenation. We do not claim a process for producing butadiene as described and claimed in this prior specification.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that subject to the foregoing disclaimer, what we claim is :—

1. A process for the preparation of butadiene by dehydrogenation of butane which consists in converting butane by heating in the presence of dehydrogenation catalysts into butylene, isolating the latter from the reaction mixture, further dehydrogenating it to butadiene and isolating the butadiene from the dehydrogenation products.

2. A process for the preparation of butadiene by dehydrogenation of butane which consists in leading butane at from 500° to 600° Centigrade over aluminium oxide activated with oxides of chromium, vanadium, tungsten or molybdenum, isolating the butylene formed from the reaction mixture, further dehydrogenating it to butadiene and isolating the butadiene from the dehydrogenation products.

3. A process for the preparation of butadiene by dehydrogenation of butane which consists in converting butane by heating in the presence of dehydrogenation catalysts into butylene, isolating the latter from the reaction mixture by absorption with an aqueous solution of silver nitrate, further dehydrogenating the butylene to butadiene and isolating the butadiene from the dehydrogenation products.

4. The process for the preparation of butadiene by dehydrogenation of butane substantially as described in the foregoing Example.

5. Butadiene when obtained by the process particularly described and ascertained.

Dated this 17th day of October, 1938.

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